Figure 1. Excitation, emission, and absorption spectra for aqueous solutions of Rhodamine WT dye

IRBORNE FLUOROMETER APPLICABLE TO MARINE D ESTUARINE STUDIES *

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ABSTRACT

An experimental Fraunhofer line discriminator detected solar-stimulated yellow fluorescence (5890 A) emitted by Rhodamine WT dye in aqueous solutions. Concentration of 1 part per billion was detected in tap water 1/2-meter deep. In extremely turbid San Francisco Bay, dye was monitored in concentrations of less than 5 parts per billion from helicopter and ship. Applications include studies of current dynamics and dispersion. Potential applications of the technique could include sensing oil spills, fish oils, lignin sulfonates, other fluorescent pollutants, and chlorophyll fluorescence.

INTRODUCTION

Fluorescent dyes are widely used in tracing or "tagging" large volumes of water in studies of current flow and rate of dispersion. This generally requires gathering water samples and subsequent measurement of dye concentration by means of a laboratory fluorometer. There are probably 40,000 or more fluorometers in use in laboratories around the country, all of them used to measure fluorescence. But the Fraunhofer line discriminator (FLD) is the first known fluorometer to measure fluorescence outside the laboratory, in broad daylight, and from a remote platform.

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The first FLD was built to sense yellow fluorescence at the sodium D_2 Fraunhofer line. This was chosen to allow testing over rhodamine dyes, which fluoresce in that region. The dyes are inexpensive and suitable either for controlled laboratory tests or for airborne tests over large water bodies.

Little mention will be made of future FLD's to sense fluorescence in other spectral regions. But it is hoped that the technique will allow sensing over land as well as water targets.

Nature of the problem

Basic problems in remote sensing of fluorescence from substances dissolved in water are:

DETERMINATION OF FLUORESCENCE COEFFICIENT BY MEANS OF FLD

SODIUM D$_2$
FRAUNHOFER
LINE

SODIUM D$_1$
FRAUNHOFER
LINE

INTENSITY (PERCENT)

100
80
60
40
20
0

5888 5890 5892 5894 5896
ANGSTROMS

$$\underline{rho} = \left[\frac{D}{A}\right] - \left[\frac{D-C}{A-B}\right]$$

$$= \left[\frac{10}{95}\right] - \left[\frac{10-8}{95-75}\right] = 0.006$$

SPECTRUM OF LIGHT FROM
SUN AND SKY REACHING
UPWARD-LOOKING TELESCOPE

HYPOTHETICAL EXAMPLE:
A = 95
B = 75

INTENSITY (PERCENT)

100
80
60
40
20
0

DASHED LINE SHOWS
FLUORESCENCE IN
LIGHT FROM TARGET

SPECTRUM OF LIGHT FROM A
SLIGHTLY FLUORESCENT
"TARGET" REACHING DOWNWARD-
LOOKING TELESCOPE

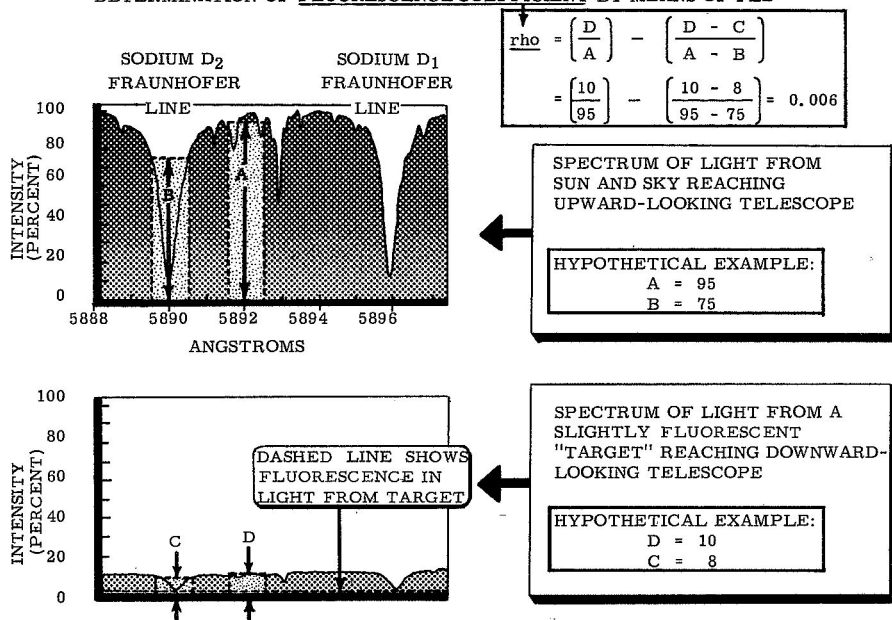HYPOTHETICAL EXAMPLE:
D = 10
C = 8

Figure 2. Determination of fluorescence coefficient by means of FLD

(1) To separate the dim fluorescence and the bright reflected sunlight coming from the same target.

(2) To correct for variations in sunlight on the target, in spite of the fact that fluorescence is increased by increasing sunlight.

(3) To record data in "real time" so that the fluorescent substance can be followed even after it is invisible to the eye.

(4) To correct for the fact that an optical sensor integrates fluorescence emanating from varying depths in the water column that it views.

(5) To convert data on fluorescence intensity, or intrinsic fluorescence of a substance, into a quantitative estimate of concentration of the substance.

(6) To plot fluorescence intensities or concentrations accurately on maps over open water, where landmarks are lacking and aerial photographs are almost useless.

Previous work on the problem

Several astronomers have used spectrometers to analyze fluorescence of the lunar surface. Hemphill (1968b) has summarized some of the findings of Kozyrev (1956), Dubois (1959), Grainger and Ring (1962), Spinrad (1964), Noxon and Goody (1965), Myronova (1965), and McCord (1967).

The present study of ultraviolet absorption and luminescence began in 1965 (Hemphill, 1968a). As part of this study, the Perkin-Elmer Corporation built the FLD. It was completed early in 1968 and has been described (Hemphill, 1968b; D. A. Markle, H. Ludwig, F. C. Gabriel, and G. Schlesinger, written communications, 1967-1968).

Objectives of recent work

Work from September 1968 to date has been summarized (Stoertz, 1969a, b, c, d). Principal objectives were:

(1) To use the FLD for estimating dye concentration in waters of varying turbidity.

(2) To use the FLD to detect dye beyond the range visible to the eye or measurable on color photographs.

(3) To develop a technique for mapping dye concentration, using the airborne FLD and a radar tracker.

(4) To obtain water samples from the air, that could be correlated with a point on the FLD record.

(5) To make a reference device for in-flight calibration of the FLD.

(6) To build equipment for testing water samples, to measure attenuation both of the incident sunlight and of the emitted fluorescence.

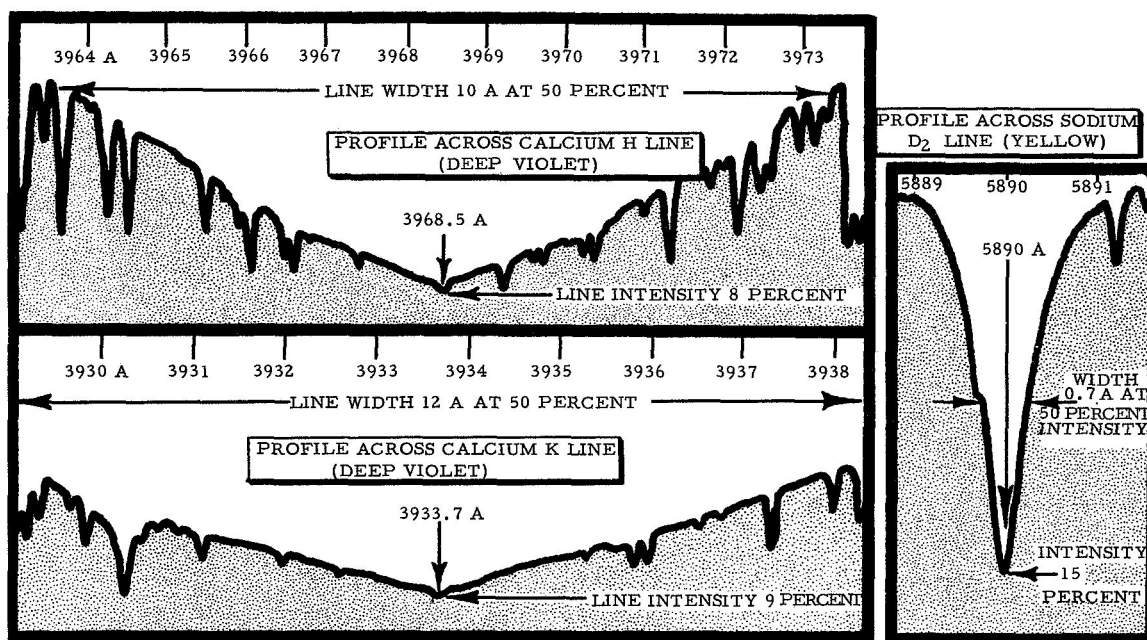In general, these objectives were achieved and results were positive.

Figure 3. Profiles across the sodium D_2, calcium H, and calcium K Fraunhofer lines

Purpose of this paper

The purposes of this paper are: (1) to outline the principle of the FLD; (2) to describe techniques for using it in airborne or shipboard surveys; (3) to summarize results and conclusions; and (4) to suggest possible applications in marine and estuarine studies.

PRINCIPLE OF THE FLD

Sunlight is highly effective in stimulating a number of substances to fluoresce. These substances emit light of their own while in a cool state, and within 10^{-8} seconds after absorbing the sun's radiation. Fluorescent brighteners in many detergents and dyes use this emission to enhance colors. The fluorescence, however, cannot normally be sensed against the bright background of reflected sunlight.

Fluorescence emission spectra

Fluorescence is *new* light and its color and intensity depend largely on properties of the emitting substance. Therefore the position in the spectrum of the peak emittance of a substance might serve to identify it if the spectral distribution of the emission could be detected. For example, the peak fluorescence of Rhodamine WT dye is between 5800 and 5820 A, as shown in Figure 1. This might serve to distinguish it from rhodamine B dye, which has a peak emission near 5780 A, or from Pontacyl Pink dye, with a peak near 5900 A (J. F. Wilson, Jr., written

communication, 1967). It should be noted that the emission spectrum (Figure 1) is the variation in intensity of emitted light with the wavelength of emitted light; the excitation spectrum is the variation in intensity of emitted light with the wavelength of absorbed light.

Reflected spectra

Normally when sunlight irradiates a substance and is partly reflected the reflected light retains a perfect but subdued image of the solar spectrum. All of the dark absorption lines that can be seen in the sun's spectrum will also appear in the reflected spectrum, as illustrated by the diagrammatic profiles in Figure 2. This is in contrast to fluorescence emission, which is characterized by broad-band spectra (e.g., Figure 1).

Solar Fraunhofer lines

These absorption lines in the sun's spectrum were identified by Fraunhofer in 1815, and subsequent detailed studies (Minnaert and others, 1940; Mohler and others, 1950) have found that they number more than 26,000. They are most prominent in the visible, near ultraviolet, and near infrared parts of the spectrum, occurring chiefly between 1850 and 17,000 A (1.7 microns). The lines result from absorption of solar radiation in the upper part of the photosphere, which is much cooler than the underlying source of the background continuum. Profiles across three of the broader lines are shown in Figure 3.
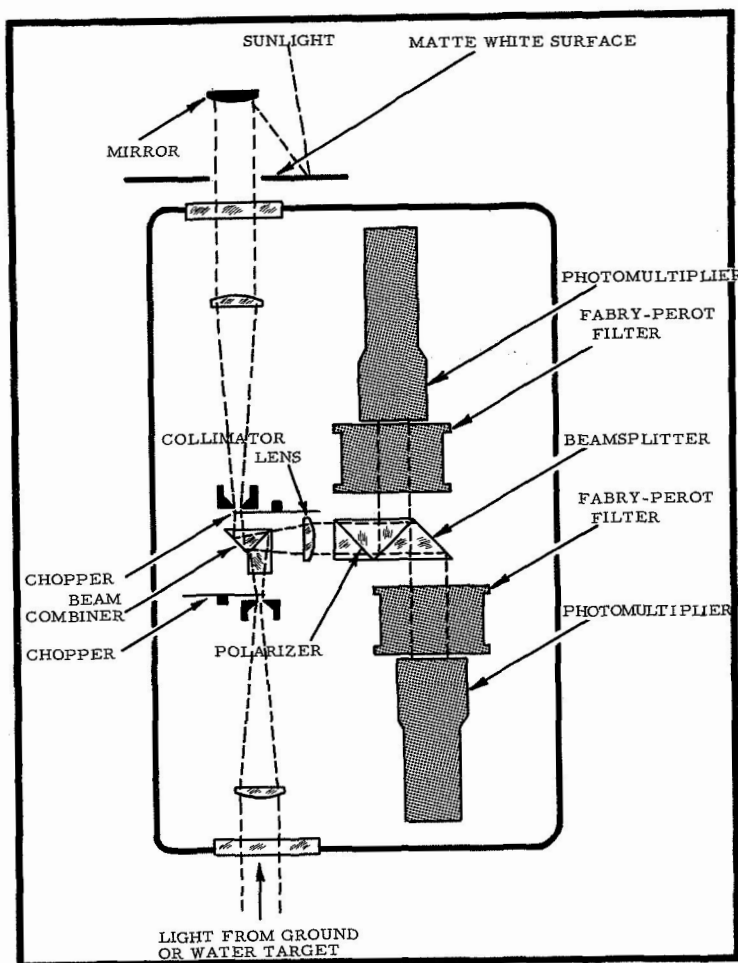
Figure 4. Diagrammatic cross section of the FLD optical unit

Fraunhofer line-depth sensing

The presence of these Fraunhofer lines in sunlight reflected from a substance makes it possible to differentiate the reflected light from any fluorescence emission that may emanate from the substance. For example, if a small amount of yellow fluorescence is present, then the Fraunhofer lines in the yellow part of the reflected spectrum will appear less pronounced than in sunlight. In effect, a dim fluorescence emission will shine through at the darkest lines and be detectable.

The FLD utilizes this principle by viewing a single Fraunhofer line in light from a substance suspected to fluoresce and comparing the relative darkness or depth of the line profile with the same line in the sun's spectrum. Any difference in the two is measured and converted into a coefficient of fluorescence of the substance.

Measured light intensities

To measure these relative line-depths and to determine the intrinsic ability of substances to fluoresce requires the measurement of four components of light (Figure 2, components A, B, C, and D). This is accomplished in the FLD by means of two Fabry-Perot filters centered at 5890 and 5892 A, each covering an average half-width of less than 1 A, represented diagrammatically by the vertical stippled bars.

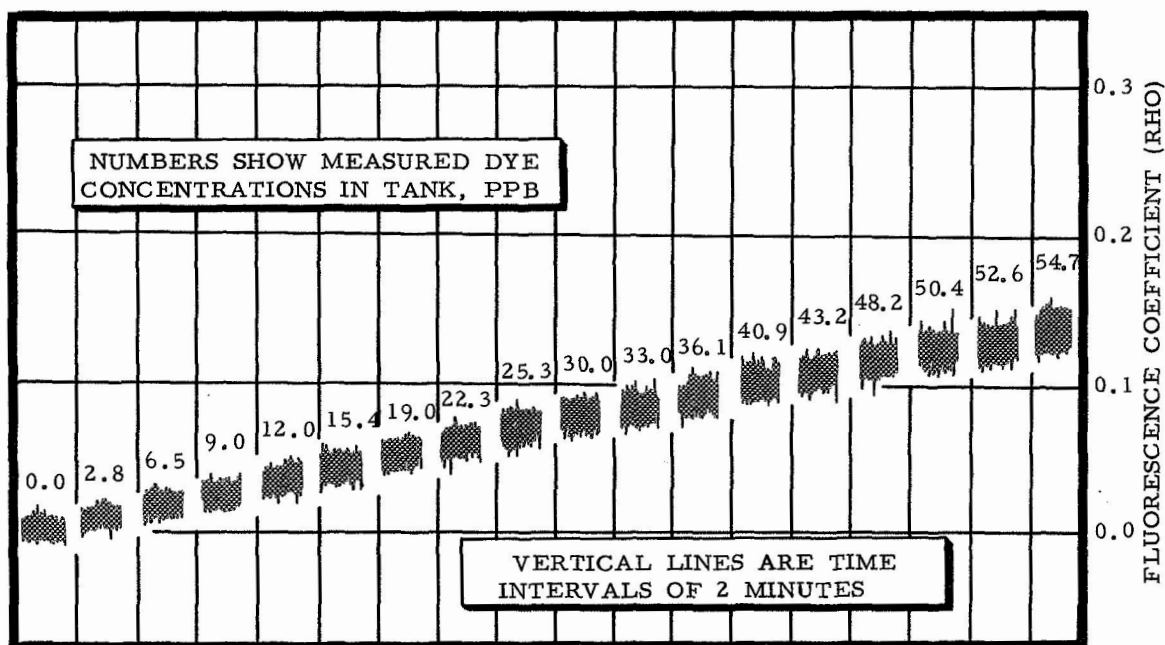The design of the instrument (Figure 4) is such that light from the sun and sky enters an upward-looking

Figure 5. FLD performance in controlled experiment over tank of fluorescent Rhodamine WT dye, October 29, 1968

telescope for comparison with light from the ground or water "target," which enters a downward-looking telescope. Light from both sources alternately passes through the two filters and its intensity is measured by photomultipliers. The four measured components are: (1) the background intensity of sunlight and skylight (designated "A"); (2) the intensity of sunlight and skylight within the Fraunhofer line (designated "B"); and (3) the corresponding intensities in light from the ground or water target (designated "C" and "D").

The profiles on Figure 2 show that light from the target is a subdued version of the solar profile. If the target is nonfluorescent in the yellow part of the spectrum, the height of shoulders and trough of the Fraunhofer line profile at 5890 A is proportional to their height in the sunlight and skylight. If the target includes a substance that fluoresces in the yellow, the fluorescence component (Figure 2, horizontal dashed line) is superimposed on the subdued profile, elevating the overall intensity without modifying the detailed notched configuration of the reflected solar spectrum. The fluorescence component can be represented by a horizontal line because fluorescence emission spectra characteristically cover a broad band of several hundred angstrom units, the intensity being practically a horizontal line as seen in any narrow band such as that in Figure 2.

Computed fluorescence coefficient

An analog computer makes a calculation approximately 20 times a second to convert the four measured light intensities (A, B, C, and D) into a signal proportional to potential fluorescence of the target. This is designated rho, or fluorescence coefficient. Rho is a measure of the intrinsic or potential fluorescence of the target, arrived at by eliminating the effects of: (1) solar intensity on the fluorescence level; and (2) variations in reflectivity of the target.

In terms of the four measured light intensities, rho is: $\left[\dfrac{D}{A}\right] - \left[\dfrac{D-C}{A-B}\right]$. Thus, the *percentage of incident light returned from the target as fluorescence* (i.e., rho) *is equal*
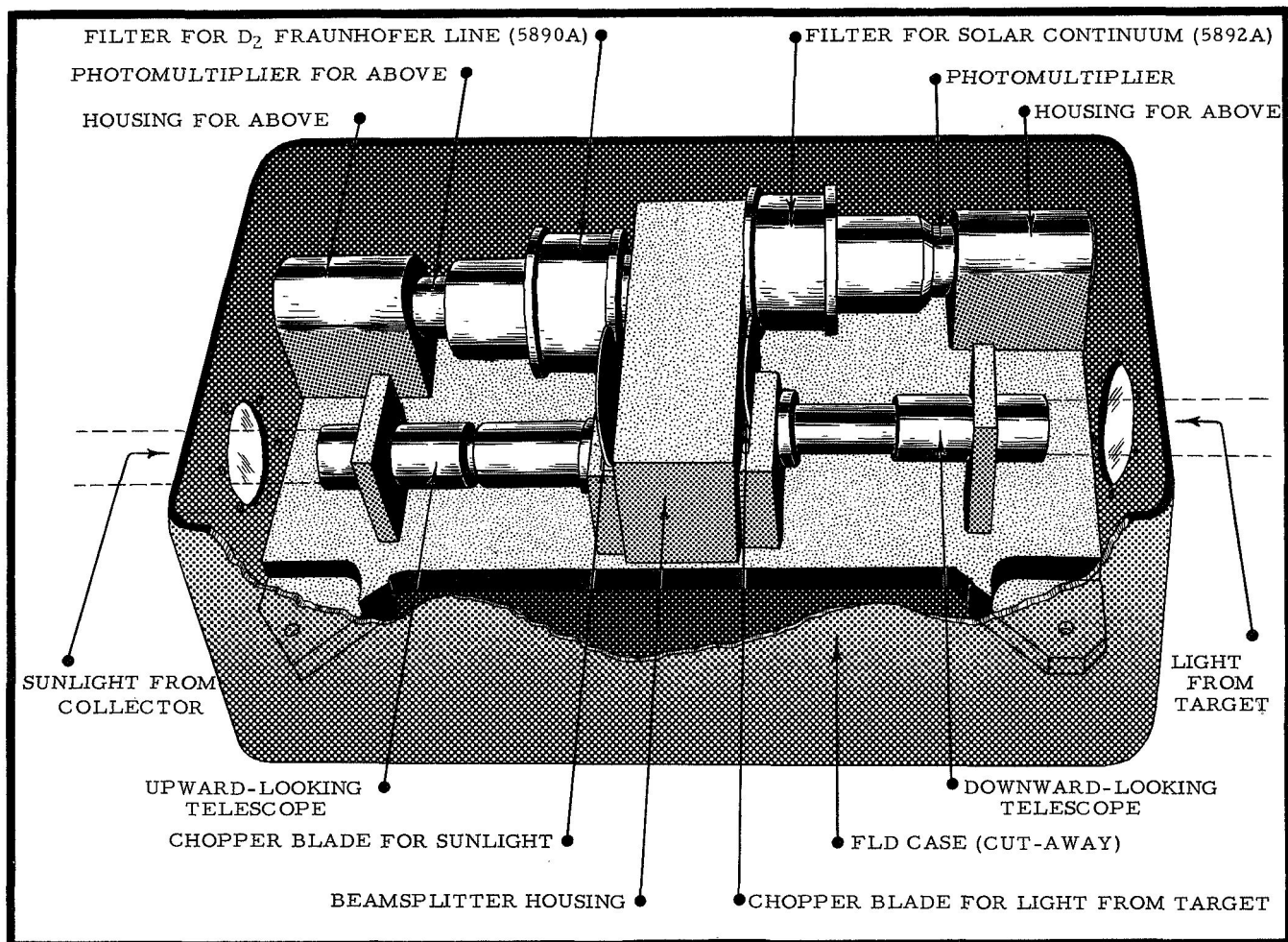

FILTER FOR D$_2$ FRAUNHOFER LINE (5890A)
PHOTOMULTIPLIER FOR ABOVE
HOUSING FOR ABOVE
FILTER FOR SOLAR CONTINUUM (5892A)
PHOTOMULTIPLIER
HOUSING FOR ABOVE
SUNLIGHT FROM COLLECTOR
LIGHT FROM TARGET
UPWARD-LOOKING TELESCOPE
CHOPPER BLADE FOR SUNLIGHT
BEAMSPLITTER HOUSING
DOWNWARD-LOOKING TELESCOPE
FLD CASE (CUT-AWAY)
CHOPPER BLADE FOR LIGHT FROM TARGET

Figure 6. Principal components of the FLD optical unit

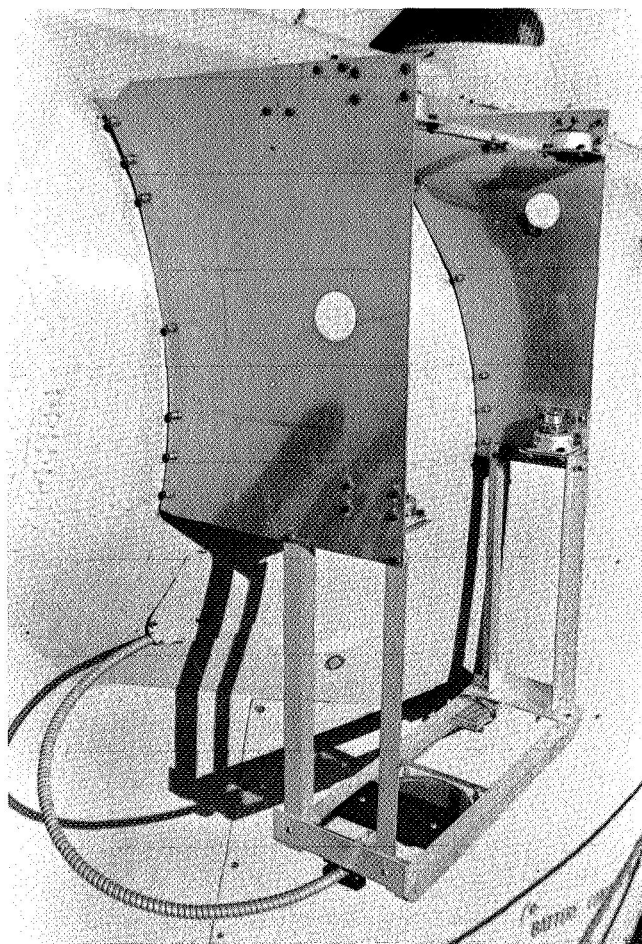**Figure 7. Mounting of the FLD on an H-19 helicopter**

Figure 8. Mounting bracket

to the total percentage of incident light returned from the target $\left[\frac{D}{A}\right]$ minus the percentage returned as reflectance and back-scatter $\left[\frac{D - C}{A - B}\right]$.

Experimental verification

To verify that the FLD functioned in accord with the foregoing principles, initial experiments with the instrument were done over a 250-gallon tank of water (Hemphill, 1968b; Stoertz, 1969c). Rhodamine dye was added in equal increments to achieve concentrations up to about 100 ppb, which were verified by analysis on a laboratory fluorometer. A strip-chart record from one of these early controlled experiments is shown in Figure 5. The pen was raised each time dye was added and stirred. Steps shown on the chart averaged 3.2 ppb. During other experiments, the smallest detectable increments of dye in 1/2-meter depths were approximately 1 ppb. The series of experiments verified that the FLD measures intrinsic fluorescence of a target, largely eliminating the effects of varying solar intensity and varying reflectivity.

APPARATUS

The FLD consists of an optical unit and an electronic console, which have been described (Hemphill, 1968b). Key optical elements (Figure 6) are two sensitive photomultipliers and two glass-spaced Fabry-Perot filters. A half-width less than 1 angstrom was achieved in the filters, making possible the high spectral resolution required to selectively view light within a single Fraunhofer line. Filters of this resolution should be capable of measuring intensities less than 50 percent of the intensity of the background continuum in approximately 75 Fraunhofer lines between 3300 and 17000 A (Minnaert and others, 1940; Mohler and others, 1950). Success of the method depends on measuring a low intensity of light within the trough of the Fraunhofer line. Intensities of about 75 percent are measured at the D_2 line (Figure 3) by the filter in the FLD. A filter of the same resolution could measure a much lower intensity in broader lines such as the calcium H and K lines in the deep violet, at 3933.7 and 3968.5 A (Figure 3). Therefore the present FLD application constitutes a "worst-case" test of the Fraunhofer line-depth method.

FLD attachments

The optical unit is mounted on the starboard side of an H-19 helicopter (Figure 7), at the point where the fuselage narrows. This position permits water sampling from the door. At ground speeds up to 15 knots a sample can be obtained close to the field of view, which is approximately a 12-inch circle at a height of 60 feet (i.e., an arc of 1°). The FLD is supported from the mounting

bracket (Figure 8) by four shock-mounts. An insulated jacket protects the optical unit from overheating in the sun.

Easily removed attachments focus sunlight into the FLD, and several kinds of light collectors have been used. The most suitable light collector (Figure 9), both for ground or airborne use, consists of a horizontal white diffuser plate 10 inches above the upper portal of the optical unit. A concave mirror supported by three rods focuses light from the collector downward into the upward-looking telescope. The off-center mounting shown in Figure 9 compensates for a prism that blocks part of the upward field of view.

An aluminum slide 18 inches beneath the optical unit (Figure 8) permits a standard fluorescent target to be periodically moved into the field of view during flight by means of an aluminum rod encased in BX-cable. This accessory is referred to as the standard target device. The most satisfactory target was an acrylic resin cylinder 1/2-inch deep and 4 inches in diameter filled with dilute Rhodamine WT dye solution. The target is shielded from sunlight by an aluminum cover when not in use, to minimize heating. The temperature of the liquid is taken before take-off and after landing to correct for decreased fluorescence with increased temperatures. The container must be viewed during straight and level flight so that sun angle is known, and it must be leak-proof, clean, and free of bubbles. The container must be shallow enough and wide enough for the column of liquid within the field of view to be fully illuminated by sunlight.

Figure 9. Light collector

Water samplers

Water samples were obtained during flight by using samplers made from sections of plastic core liner (2 in. I.D.) and fastened with wire (Figure 10). The samplers hold a 6-ounce widemouthed bottle. That volume is sufficient for measuring attenuation coefficients with the apparatus described below. Amber-glass bottles are used to retard deterioration of rhodamine dye in the sunlight. Bottles will not drop out and they can be changed in a few seconds. Expendable weights can be used to adjust drop-angle for varying ground speeds and altitudes, in order to sample close to the field of view during flight.

During 20 hours of airborne and shipboard tests of the FLD in May, water samples were taken on an average of once every 6 minutes in order to calibrate the instrument and verify dye concentrations. Closely spaced samples were frequently desired to establish an adequate profile across a single dye cloud. Single samples were taken in as little as 18 seconds from the ship and as little as 25 seconds from the helicopter. During more recent tests the standard target device has been used instead of samples in order to calibrate the FLD. As a result, water samples are needed less
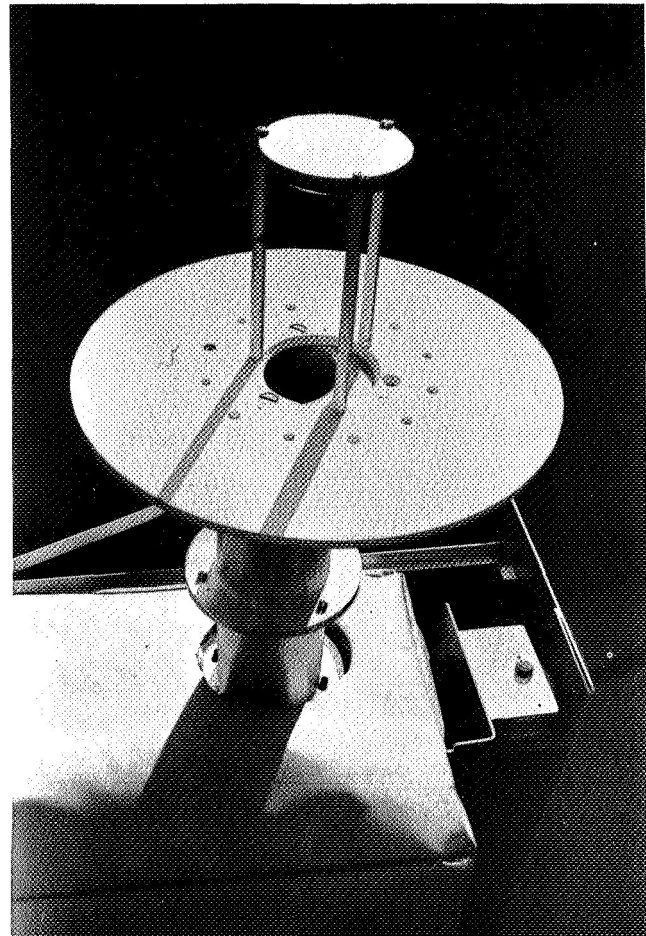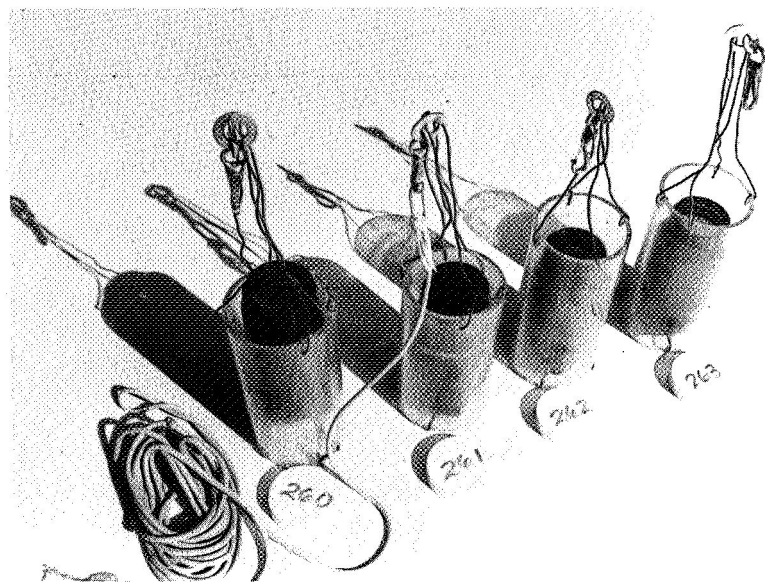

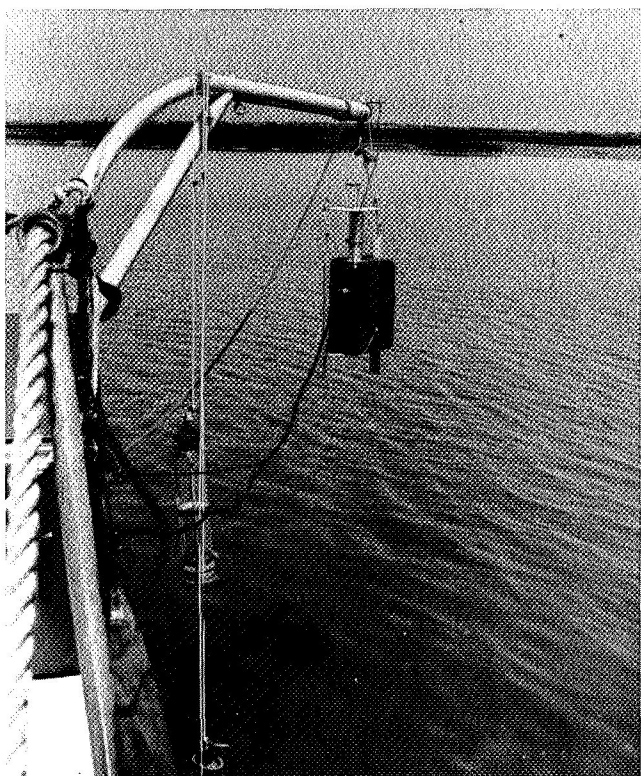Figure 10. Expendable samplers holding 6-ounce bottles

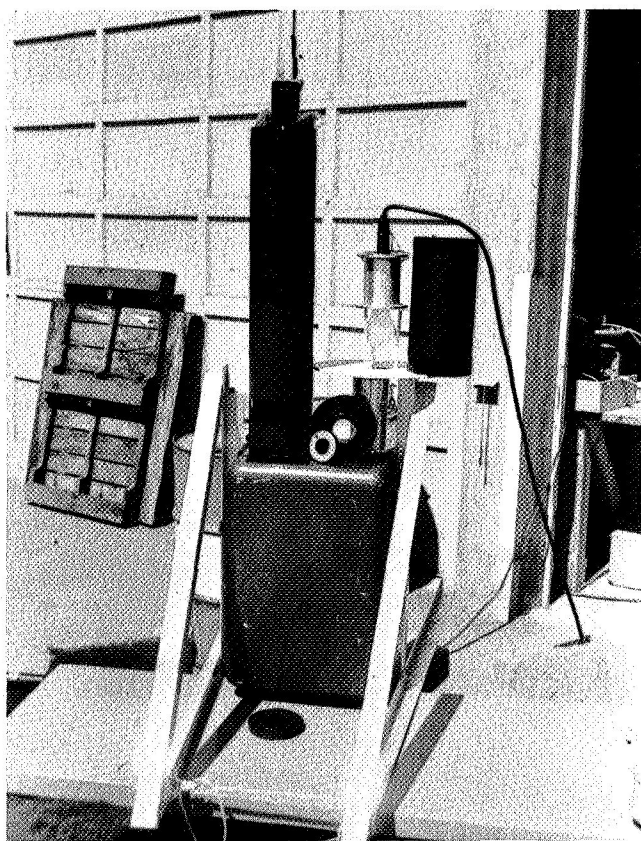**Figure 11. Subsurface samplers in use aboard** *Polaris*

Figure 12. Apparatus for measuring attenuation of emitted fluorescence at 5890 A

frequently and mainly to measure attenuation of light by suspended particles and other constituents in the water.

During shipboard tests some subsurface samples were taken in standard bottles rigged for simultaneous sampling at pre-determined depths of 1, 2, and 4 meters (Figure 11). Such sampling makes possible the estimation of vertical distribution of turbidity and of dye in the water column viewed by the FLD. It has not been needed in most waters tested to date because light penetration has been shallower than 1 meter. However subsurface sampling will be essential in future use over clearer ocean water, and a simpler device may be required for this purpose.

Attenuation measurement apparatus

Improvised apparatus (Figure 12) permits measurement of attenuation of yellow fluorescent light by the water sampled. Artificial light is passed through a long tube of the sampled water into the upper portal of the FLD, where its intensity at 5890 A is measured. For comparison, the same thing is done for distilled water and for standard solutions of Rhodamine WT dye in concentrations of 50 and 100 ppb. Three sample tubes of black acrylic resin having clear bottoms are provided so that the path-length can be varied from 8 to 20 inches, according to sample size and water clarity. The test requires only 5 minutes per sample, and can be done indoors when outdoor work is not possible.

Attenuation of those wavelengths of incident sunlight that serve to excite the yellow (5890 A) fluorescence of Rhodamine WT dye is measured by a modified apparatus (Figure 13). These wavelengths are in the green part of the spectrum, since absorption by the dye is chiefly in the green as shown by the excitation or absorption spectra (Figure 1). However, the range of wavelengths varies with depth in the dye solution and with dye concentration. In this application, the sunlight is reflected down through a sample by a mirror. The portion that is transmitted serves to excite fluorescence in a small cylinder of Rhodamine WT dye that is viewed at a right angle by the lower telescope of the FLD. The upper telescope monitors the incident sunlight, as in conventional use, so that fluorescence coefficient (rho) can be computed by the FLD. This gives a measure of the attenuation, by the sample, of those wavelengths which cause the dye to fluoresce.

Both types of attenuation apparatus described above use the FLD optics. Therefore the measurements are uniquely suited to sensing at the specific wavelengths of the FLD filters (approximately 5890 and 5892 A) and provide results not possible by other methods.
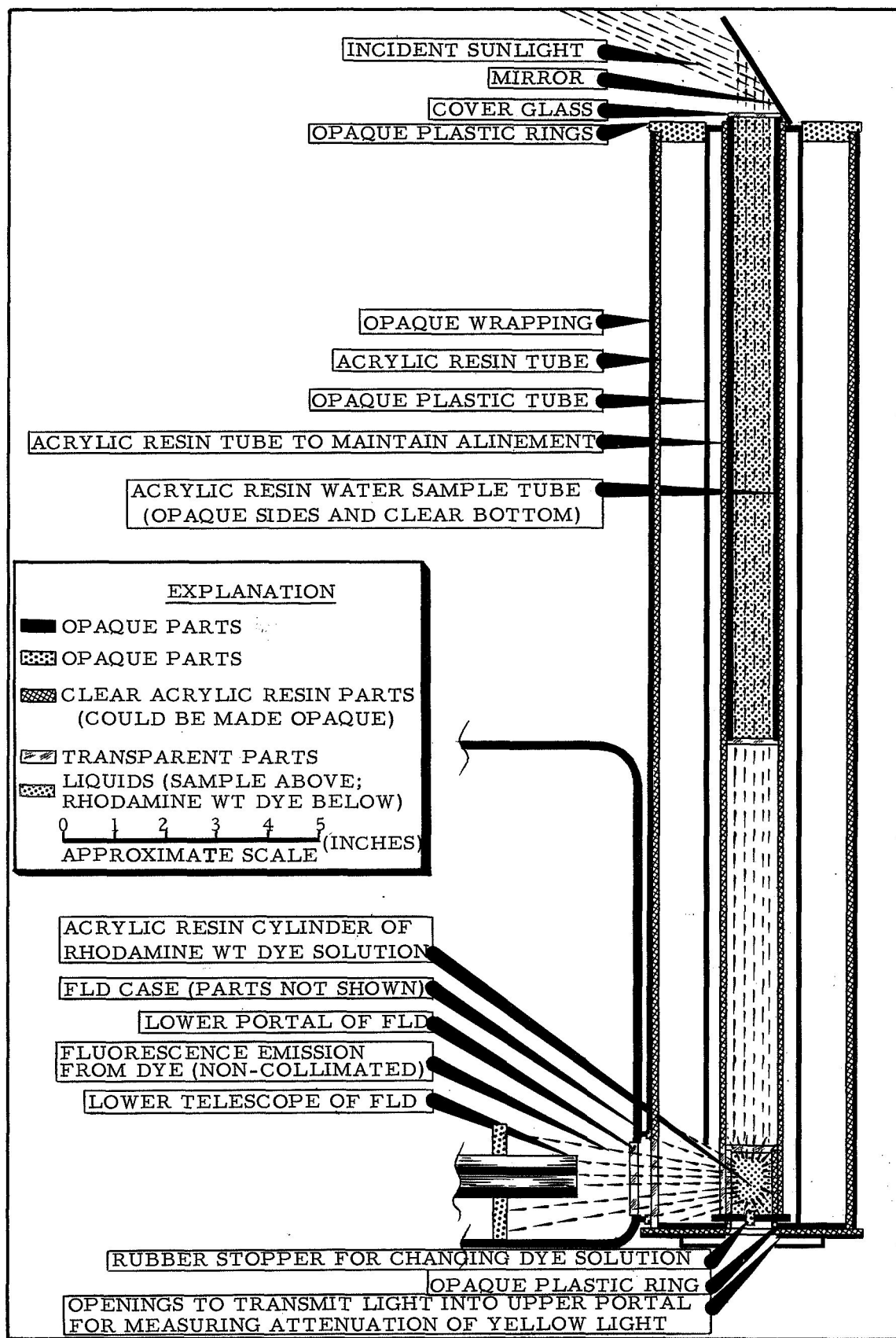
Figure 13. Apparatus for measuring attenuation of incident sunlight that excites fluorescence of Rhodamine WT dye at 5890 angstroms
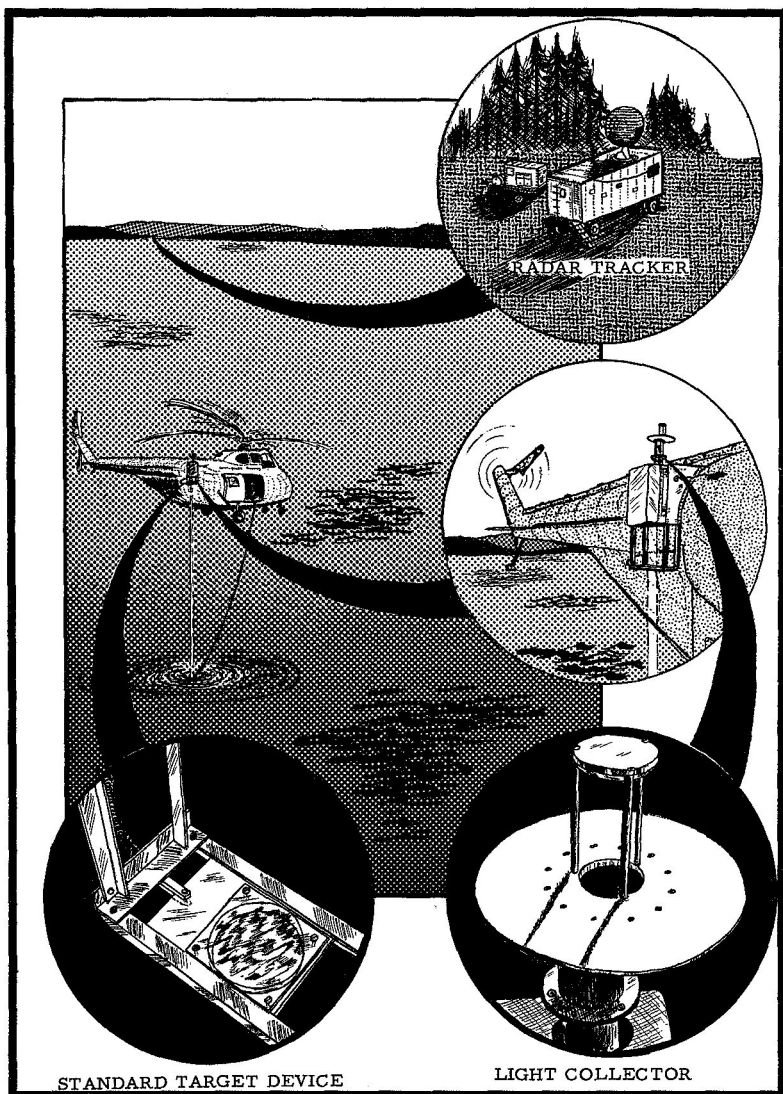
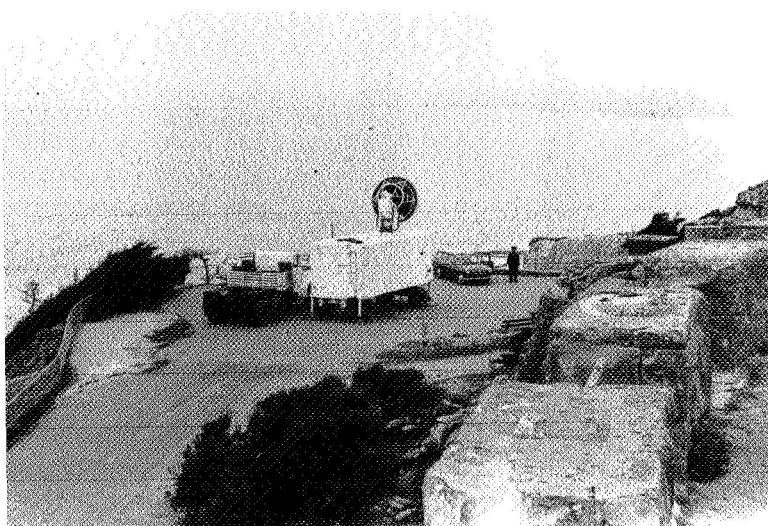Figure 14. Sketch of FLD mounted on H-19 helicopter for survey over water

STANDARD TARGET DEVICE   LIGHT COLLECTOR

RADAR TRACKER

Figure 15. Radar tracker at Point Lobos, looking toward test site near Golden Gate

SURVEY METHODS OVER WATER

Among the useful applications of the FLD over water will be the development of contour maps showing areal distribution of fluorescent dye concentrations in water bodies. The speed at which the airborne FLD system can sample for concentrations or spatial distributions is expected to make it superior to conventional methods for mapping such short-lived and ever-changing phenomena. Recent work has focused on developing procedures for this. A sketch of the FLD in use during an airborne survey over water is shown in Figure 14.

The airborne survey party consisted of one or two persons in addition to the pilot. They air-dropped dye in the water, operated the standard target device, photographed dye while it was visible, recorded time on strip-chart, marked sample locations and the edges of visible dye on the chart, took water samples, and measured water temperature.

A modified radar fire-control system was used as a tracking radar, and located within 15 miles of the test area. The radar van (Figure 15) was manned by one person (Howell, 1969) who plotted the precise flight path on maps, marked the location of dye as relayed by radio, recorded time ticks to enable ground speed determination, communicated time checks to the pilot by radio, and frequently helped navigate the aircraft near the dye when it was practically invisible to the pilot. This was possible because the radar operator had before him a plot showing the previous location of the dye cloud. Radar sites used between May and August 1969 are shown on Figure 16. The installation at Point Lobos is shown in Figure 15; a survey with the FLD was made over the water in the background.

A suitable method for air-dropping dye is a double plastic bag released from a stiff widemouthed container. Breakage at the water surface is assured by excluding air and dropping from 100 feet or higher. When a radar tracker is not available to correct for true ground speeds, dye patches can be used, in conjunction with aerial photography from a higher aircraft. Small dye spots are dropped from the survey aircraft to mark the beginning and end of cross-traverses of a larger dye cloud, and the exact locations of these marker patches are noted on the FLD strip chart. Then the true lengths of the traverses can be plotted from photographs taken at a higher altitude, providing the marker patches are visible. A Cessna 310 was used for this purpose during FLD tests.

FLD operation

The FLD is turned on at take-off to allow warm-up time. It operates at 110-v. A.C. produced by a generator that operates from the 24-v. aircraft power. A continuous record of solar intensity (component A on Figure 2) and fluorescence coefficient (rho) is produced on a dual-pen strip-chart recorder, using a bandwidth of 2 Hz for both. Suitable recorder ranges are 1X for component A and 10X for rho. A chart speed of 0.1 inch per second is suitable while flying over dye.

The FLD can also operate as a shipboard fluorometer. It was suspended from a davit on the Geological Survey ship *Polaris* (Figure 17). Successful performance was proven by sampling at frequent intervals at a point adjacent to the field of view, and this also permitted frequent calibration of sensitivity.

ESTIMATING CONCENTRATIONS WITH FLD

In the course of early testing, comparison of charts made from one day to another (e.g., Figure 5) showed that a given value of fluorescence coefficient (rho) might correspond to many different dye concentrations. It was evident that a number of factors other than dye concentration entered into the recorded values of rho. Rho, then, is analogous to the dial reading of a fluorometer, and might better be termed FLD reading instead of fluorescence coefficient. Interpretation of these readings in terms of either fluorescence intensities or dye concentrations requires that pertinent environmental factors and internal instrumental factors be considered.

First, the entire water column viewed by the FLD must be considered. As calculated by the analog computer in the FLD, rho is approximately equal to the relative intensity of upward-trending fluorescence reaching the water surface from the column sensed by the FLD, after being attenuated by absorption and scattering by all constituents of the column: (1) suspended particles; (2) the water; (3) the dye; and (4) other coloring matter. The incident sunlight whose intensity is measured at the light collector is similarly attenuated by all constituents as it slants downward through the water before reaching the vertical column viewed by the FLD, where it stimulates the fluorescence sensed by the instrument.

The principal environmental factors affecting rho are angle of the sun's rays, temperature of the water column, vertical distribution of the dye, and attenuation of light by all constituents of the water. Rho also depends on internal instrumental factors that cannot be separately evaluated. These are combined into a sensitivity coefficient that is evaluated periodically by viewing standards, to relate
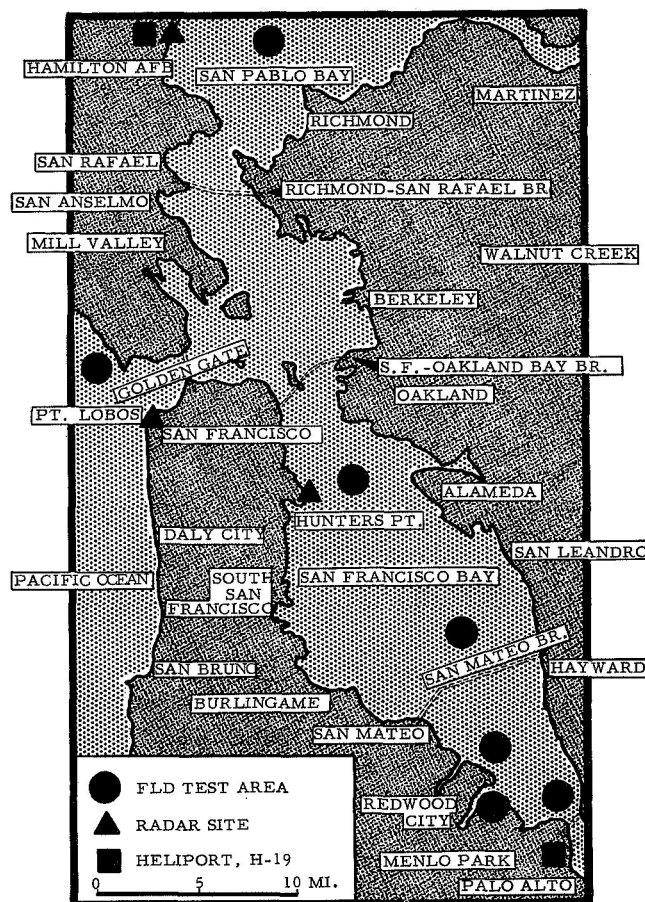

Figure 16. Index map of FLD test areas and radar sites, May to August, 1969
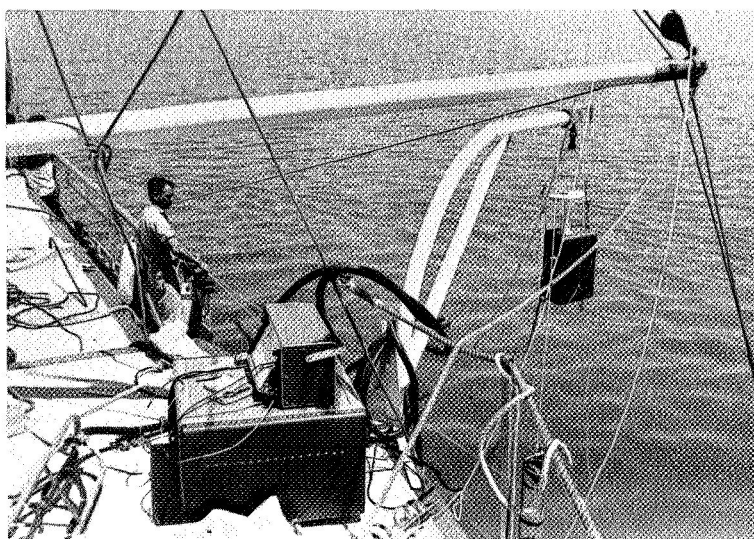

Figure 17. Use of FLD as shipboard fluorometer aboard Geological Survey ship *Polaris*
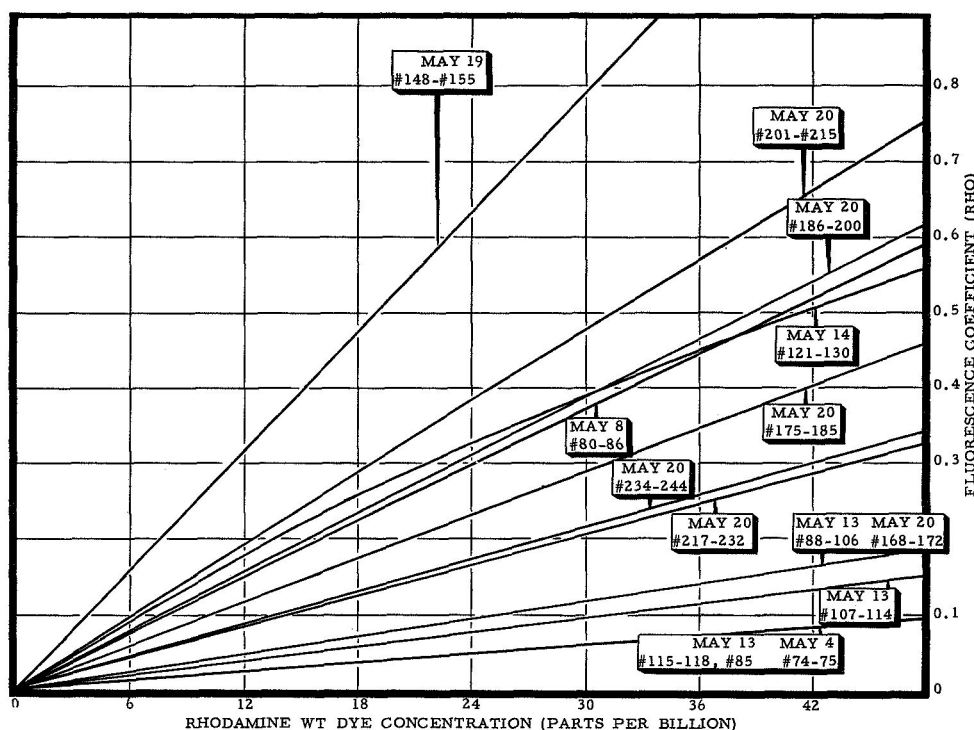
Figure 18. Relation between dye concentration and FLD readings for short test periods

instrumental sensitivity to increments of the fluorescent substance. This coefficient is basically the increment in rho produced by the fluorescence from an infinitely small quantity of a fluorescent solution divided by that quantity. The coefficient also includes an error factor to compensate for the cumulative error from indeterminate sources.

Theoretical formulas have been derived relating the

above factors to rho (Stoertz, 1969b). Average dye concentrations within the column viewed by the FLD can be estimated by using these formulas, although several assumptions are necessary. For example, it must be assumed that the dye is uniformly dispersed with depth.

A graphical plot (Figure 18) of rho values versus calculated average dye concentrations aids in scaling the
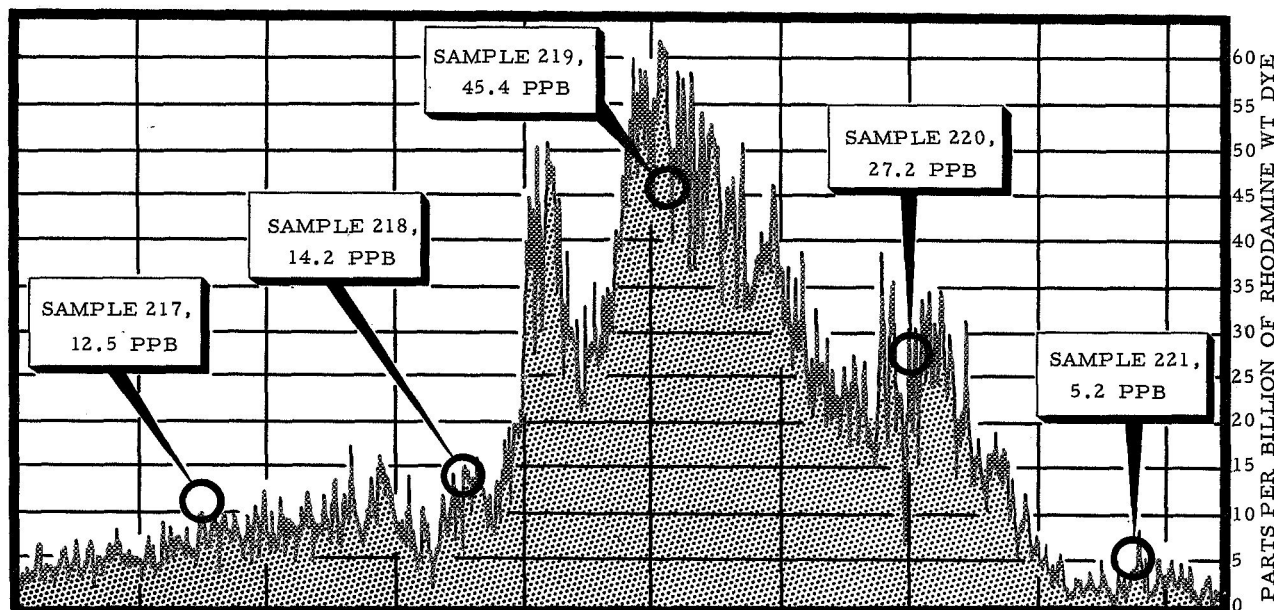
(VERTICAL LINES ARE TIME INTERVALS OF 10 SECONDS)

Figure 19. Record from FLD used as shipboard fluorometer, San Francisco Bay, May 20, 1969

strip-chart records to read directly in terms of dye concentration. The curves illustrated are for a number of short test periods in May, averaging 10 minutes in duration, during which the variables of sun angle, turbidity, and instrumental sensitivity appeared nearly constant.

A typical FLD record showing the final scaling by horizontal ruled lines is illustrated by Figure 19. A period of significantly lower sensitivity occurred during tests near Redwood City (Figure 20). Higher sensitivity was recorded over San Francisco Bay north of San Mateo Bridge (Figure 21), and that record also illustrates the limitation of pen response time. The uniform slope of all peaks apparently results from this factor.

Very high sensitivity occurred over the Pacific Ocean near Golden Gate (Figure 22). The high sensitivity is attributed to clear water and possibly deep dispersal of dye. The FLD readings could not be interpreted by formula, probably because the lowermost portion of column viewed extended deeper than the lower limit of the dye. In this case, subsurface samples would be needed. However, surface samples analyzed by a laboratory fluorometer showed concentrations of 0.5 and 1.4 ppb, suggesting that a sensitivity lower than 0.5 ppb was achieved.

CONCLUSIONS AND RECOMMENDATIONS

(1) Controlled experiments over tanks of Rhodamine WT dye in aqueous solutions showed that the smallest
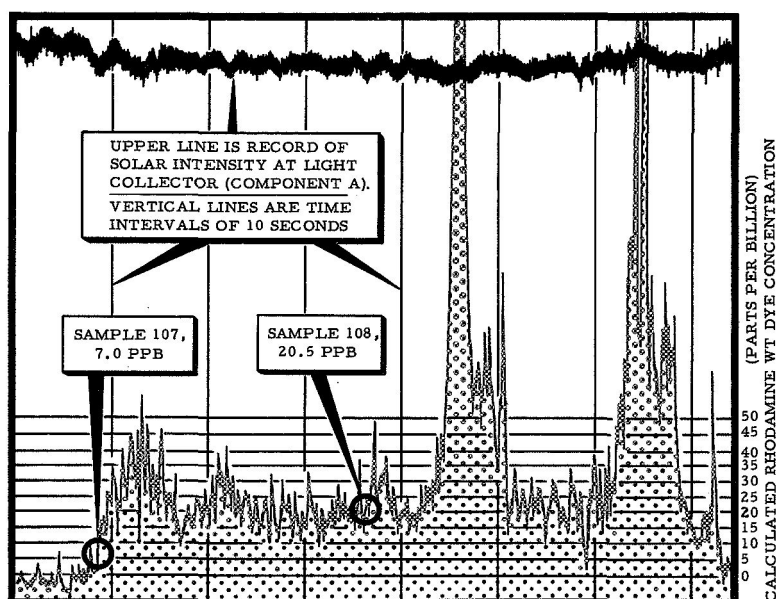

Figure 20. Record from FLD used as airborne fluorometer, San Francisco Bay, May 13, 1969

detectable increment of dye in 1/2-meter depths was approximately 1 ppb. During an experiment on November 2, 1968, between 11:23 and 11:52 a.m., 25 successive increments averaging 1.3 ppb were clearly differentiated (Stoertz, 1969c).

(2) Tests showed that illumination of the dye column sensed by the FLD is more important in determining rho values than how much dye is in the column, although the two are interrelated. Therefore attenuation
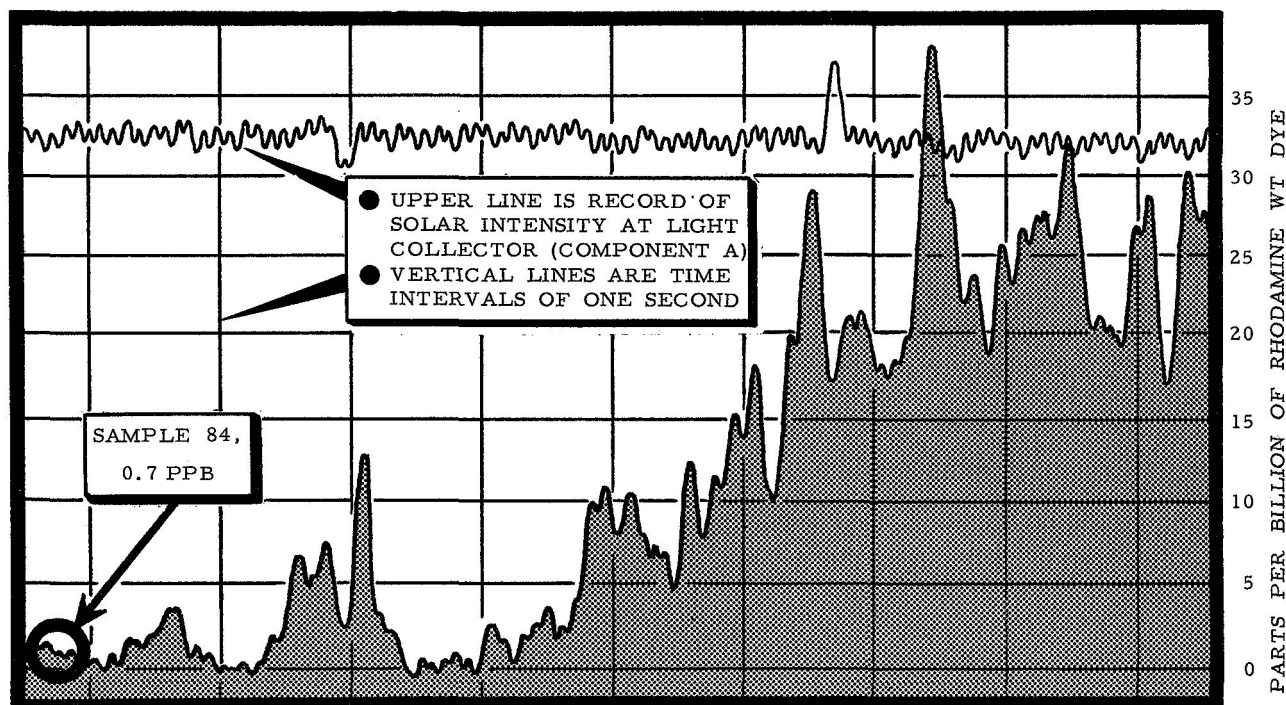

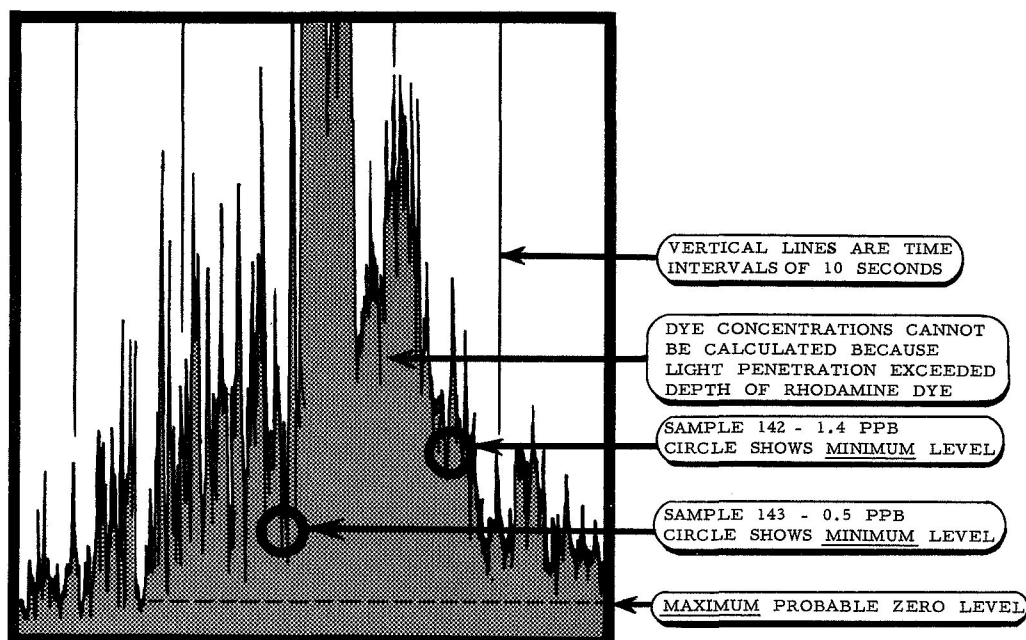Figure 21. Record from FLD used as airborne fluorometer, San Francisco Bay, May 8, 1969

Figure 22. Record from FLD used as airborne fluorometer, Pacific
Ocean near Golden Gate, May 14, 1969

coefficients for light are the principal factors to be considered in interpreting FLD records.

(3) Tank tests over dye dissolved in clear water in which attenuation of fluorescence is isolated from that of incident light showed a nearly direct proportionality between rho values and fluorescence intensity for varying depths. Laboratory experiments also indicated that attenuation of yellow light by Rhodamine WT dye is slight relative to attenuation by suspended particles. Therefore, in most natural water bodies, self-absorption of fluorescence by rhodamine dye appears to be negligible when compared to absorption by the suspended particles.

(4) Absorption of green light by rhodamine dye was much greater than was the case for yellow light. However absorption of green light by suspended particles in the turbid waters of San Francisco Bay was many times greater than that of a 100-ppb dye solution. Therefore the most critical factor to consider in interpretation of FLD records is generally turbidity of the water, and its effect on light attenuation.

(5) Tests of temperature-dependence of fluorescence have shown that this factor is significant and cannot be overlooked in quantitative use of the FLD. If temperature variation with depth is known the average should be weighted to correspond to the average depth from which fluorescence emanates.

(6) Tests of the relation between reflectance of target materials and recorded rho values suggest that when reflectivity exceeds some critical limit the FLD computer cannot cope with the signal and a spurious rho value is recorded. This limit appears sufficiently high that reflectance is generally not a problem during level flight over water. The critical limit appears to be exceeded only during low sun angles, high surface roughness, and when the aircraft banks toward the sun in turning.

(7) Shipboard and helicopter tests of the FLD for measurement of fluorescent dye in water were successful, as
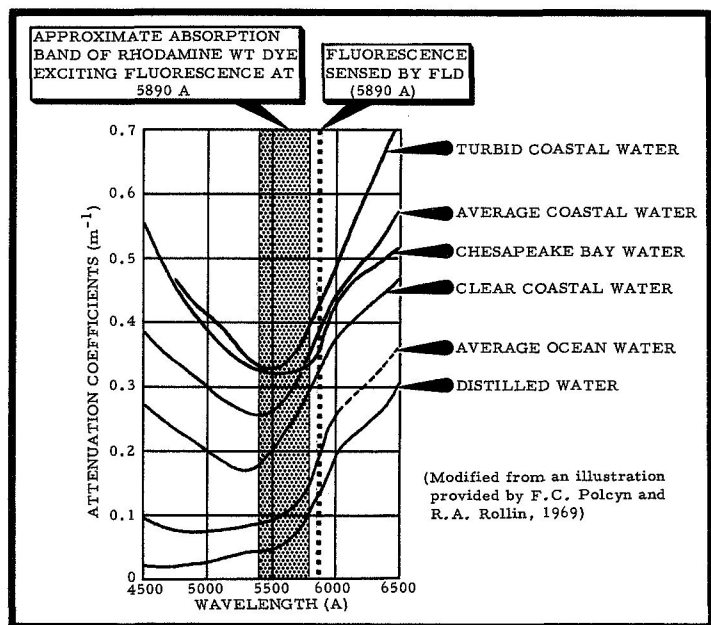

Figure 23. Relation of light attenuation to FLD function when sensing Rhodamine WT dye in water
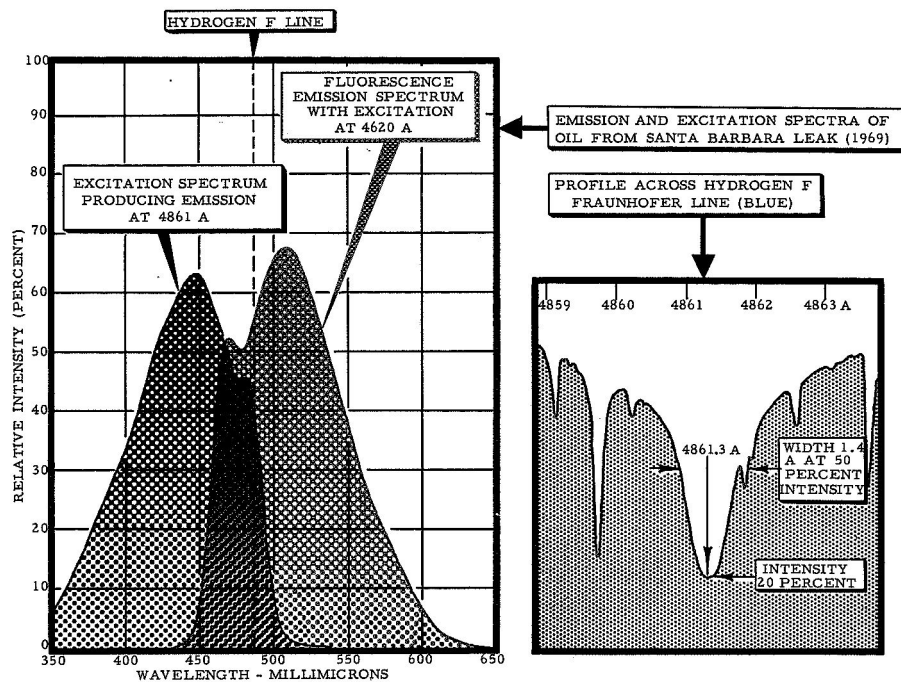
Figure 24. Fluorescence of Santa Barbara oil leak in relation to spectral region of sensing by planned future FLD

was the plotting of flight paths by tracking radar. These two techniques, used together, are promising.

(8) Water sampling procedures for use during remote sensing by the FLD were devised and successfully tested. An apparatus was built to permit measurement of attenuation of incident sunlight and emitted fluorescence by selected samples.

(9) Airborne tests up to altitudes of 5,000 feet were conducted over clouds of rhodamine dye. As altitude increased the highest peaks recorded by the FLD were flattened due to increasing size of the field of view, but the dye was clearly detectable at the highest altitude reached.

(10) On clear sunny days the optimum time for sensing with the FLD is during the 6-hour period centering at midday, but sensing of rhodamine dye has proved successful as late as 5:45 p.m. local time during August, or approximately 4 3/4 hours after sun's transit. Since fluorescence is greatest at highest sun angles, the best time of year north of latitude 23 1/2°N. is near June 21 from the standpoint of sun angle alone. During spring and summer months at mid-latitudes the period suitable for sensing will probably average about 8 hours per day on clear sunny days.

(11) A comparison of FLD records for equal concentrations at varied times shows that significant changes in sensitivity occurred and illustrates the necessity of repeated calibration by viewing fluorescent standards during flight. A

new design for a future FLD, having only one photomultiplier, should essentially eliminate problems of varying sensitivity and eliminate the need for monitoring standard targets.

(12) Exceptionally high sensitivity was noted during tests over the Pacific Ocean near Golden Gate, as a result of relatively clear water. In areas of well dispersed dye the sensitivity appeared great enough to differentiate increments of rhodamine dye smaller than 0.5 ppb. This finding is very encouraging but also indicates the necessity of sampling subsurface waters during use of the FLD. A limitation of the present method is the assumption that the dye is uniform throughout the water column sensed. Therefore an improved means for subsurface water sampling from a helicopter is needed.

(13) When used for sensing rhodamine dye in coastal waters and estuaries the FLD will by design be sensing in the spectral region permitting nearly maximum depth of light penetration. This is shown in Figure 23, which was modified from an illustration provided by F. C. Polcyn and R. A. Rollin, Willow Run Laboratory, University of Michigan. The FLD appears nearly optimum for sensing in turbid estuaries such as Chesapeake Bay or San Francisco Bay. It appears to have an advantage over conventional dye sampling and fluorometer analysis methods in that it adds the dimension of depth, and the greater mobility of aircraft operations.

(14) A future FLD could operate at a different Fraunhofer line, such as the hydrogen F line (4861 A) in

the blue part of the spectrum. As illustrated by Figure 24, that line falls near the fluorescence emission peak of oil from the Santa Barbara leak. The present FLD, at 5890 A, failed to detect the oil in a series of tests. The line profile (Figure 24) shows that a filter similar to those in the present FLD could probably measure light intensities as low as 50 percent of the background continuum; the limit at the sodium D_2 line of the present FLD seems to be about 75 percent. A future instrument might also operate at a line in the red, for detection of chlorophyll fluorescence. A future FLD could be a versatile sensor suitable for such applications as monitoring oil spills and leakages, algal blooms in water bodies as an indicator of pollution, and dispersion studies based on fluorescent dye.

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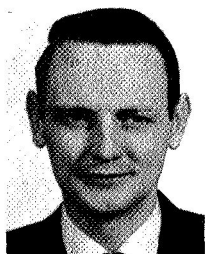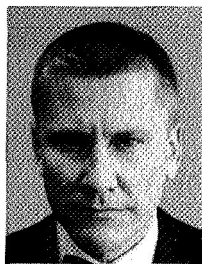
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